SPATIAL VARIATION AND CHARACTERISTICS OF VOLATILE ORGANIC COMPOUNDS ASSOCIATED WITH SNOWMOBILE EMISSIONS IN YELLOWSTONE NATIONAL PARK

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Abstract

Preliminary results of a spatial investigation of emissions associated with oversnow travel in Yellowstone National Park on February 13 and 16, 2002, are presented. The National Park Service is currently engaged in the task of developing regulations for improving air quality in Yellowstone National Park with the primary intentions of reducing human exposure to toxic air pollutants and improving visibility. While the NPS is drawing upon the results of an extensive body of research, to date, no previous investigation has focused specifically on the issue of the spatial variability of snowmobile emissions. Ninety-six whole air samples whose locations were georeferenced using global positioning system receivers/data loggers were analyzed using gas chromatography with flame ionization and electron capture to determine the mixing ratios of some 95 volatile organic compounds. Utilizing a geographic information system to show the extent of oversnow vehicle emissions in Yellowstone National Park, the findings indicate that two-stroke snowmobile engines appear to contribute large quantities of hydrocarbons, including air toxics, to the airshed.

1. Introduction

This report summarizes the findings of an intensive study of the spatial distribution of volatile organic compounds (VOCs) associated with oversnow vehicular travel in Yellowstone National Park (YNP) during February, 2002¹. The report constitutes a set of preliminary findings and is being submitted for consideration by the National Park Service (NPS) in its capacity as lead agency in the development of winter use plans for the Yellowstone and Grand Teton National Parks, and the John D. Rockefeller, Jr., Memorial Parkway, as required by settlement agreements² established with litigants in 1997 and 2001. The investigators have the fullest confidence in the findings reported, and the preliminary nature of the report owes to consideration of a more limited set of VOCs than were resolved in the laboratory. The investigators intend to submit a more comprehensive set of findings in the future in the form of either an additional report or a draft manuscript to be submitted for publication in a peer-reviewed scientific journal.

1.1 Overview of Investigation

As described in the research proposal submitted for approval by the YNP Research Permit Office, the investigators acquired whole air samples for analysis throughout the Park on February 13 and 16, 2002. The dates selected (Wednesday and Friday, respectively) were selected to coincide with both lower- and higher-traffic days associated with the President's Day Weekend which has historically represented a high-visitation period during the Park's winter season [*J. Sacklin*, Personal Communication,

¹ YNP investigation: "Spatial variation and characteristics of volatile organic compounds associated with snowmobile emissions in Yellowstone National Park" (YNP Research Permit No. 5266).

² These settlement agreements led to the development of a Final Environmental Impact Statement (10/10/2000) and associated Record of Decision (11/22/2000) and Final Rule (1/22/2001), and Supplemental Environmental Impact Statement (In Review, 3/29/2002).

2001]. A total of ninety-six whole air samples were acquired in evacuated steel canisters. They were distributed among morning, afternoon, and diurnal sample sets acquired for each day. The locations of the samples were registered with global positioning system (GPS) units, and their contents analyzed by gas chromatography using flame ionization and electron capture detection. In addition, exhaust emissions from both a two-stroke and a four-stroke snowmobile were sampled for comparative purposes as well as gasoline vended at the Old Faithful concession and at commercial vendors in the towns of West Yellowstone, Gardiner and Livingston, MT. The data were subjected to spatial analysis utilizing interactive graphical interpretation and mapping conducted with the use of a geographic information system (GIS). Discussions of the methodologies employed in the field and laboratory, the field conditions associated with data collection, the chemical and spatial analyses undertaken, and of our findings are presented.

1.2 Air Quality Issues in Yellowstone National Park, Previous Research, and Rationale for the Investigation

This investigation was undertaken to investigate the spatial distribution of VOCs associated with oversnow vehicular travel in YNP. Like other U. S. National Parks, YNP has been designated a mandatory Class I Airshed under the Clean Air Act (CAA), and is thus subject to the requirement that the quality of air within its boundaries remain in a pristine or high-quality state such that it does not suffer from impairment of visibility [Clean Air Act - Section 169A.a.1, 1970, 1990]. Owing to a steady increase in wintertime oversnow recreational vehicle use in the Park since the late 1960s, which has significantly increased mobile-source (i.e., snowcoach and especially snowmobile) emissions, air quality and visibility within the Park have been acknowledged to have decreased to levels that have prompted Park Managers to consider alternative regulatory strategies [National Park Service, 1999, 2000a, 2000b]. In response to the need to remedy impairment of visibility in the Park resulting from manmade air pollution as required by the CAA (Section 169A.a.1) and to address the issue of human exposure to toxic air pollutants, also mandated by the CAA and by the Occupational Safety and Health Administration (OSHA), extensive research has been conducted within the Park to characterize and quantify snowmobile emissions with respect to carbon monoxide, VOCs, and particulate matter emissions as well as their impacts on human health [National Park Service, 1995, 1996; Ingersoll et al., 1997; Snook and Davis, 1997; Radke, 1997; Carrol and White, 1999; Ingersoll, 1999; Kado et al., 1999; Morris et al., 1999; Institute for Environment and Natural Resources, 2000; Bishop et al., 2001].

While this body of research is broad in scope, the majority of work has been focused on the issue of human exposure to toxic air pollutants (i.e., VOCs and particulate matter). No study to date has explicitly documented the spatial distribution of emissions associated with oversnow travel in the Park. Furthermore, no study other than those reported by *Ingersoll et al.* [1997] and *Ingersoll* [1999] relied on more than 6 sample sites within the Park itself. The spatial variation of snowmobile related VOCs remains unknown to date [*Institute for Environment and Natural Resources*, 2000].

Based on the results of this body of research and additional studies concerning snowmobile-wildlife interaction, the National Park Service (NPS) published a Record of Decision (ROD) based on a "Winter Plans Final Environmental Impact Statement..." [2000a] which would have steadily reduced snowmobile use in the Park over the period 2001-2003 and encouraged winter visitation only via NPS-managed snowcoaches. However, the NPS has since been forced to set aside its ROD and develop additional or modified alternative courses of action for regulating oversnow travel in the Park in a Supplemental Environmental Impact Statement [*U.S. Dept. of Interior*, 2002].

Given this state of affairs, the investigators conducted a rigorous investigation of the spatial variation of snowmobile related VOCs in YNP under conditions of historically high levels of snowmobile usage. The intent of the investigation was to establish a set of baseline data associated with levels of oversnow travel that approximate historical peaks in order to document, through future studies, the effectiveness of any reduction in such travel owing to management decisions enacted by the NPS. Additionally, the investigation was intended to serve as a pilot-study designed to test the sampling and analytical methodologies for utilization in future studies to be conducted in the Park.

2. Methods

The methods involved in the acquisition and analysis of air samples, and in the spatial analysis of results are presented here.

2.1 Study Area, Sample Collection, and Field Conditions

A regular grid of 20 km² cells was superimposed over the Park to identify potential sample sites that correspond to wintertime accessible areas and to ensure complete spatial coverage (Figure 1). In addition to those samples obtained within the Park's boundaries, samples were also acquired at Silver Gate, the East Entrance, and to the south of West Yellowstone adjacent to the Park boundary (Table 1). These three sites were selected, respectively, to provide information concerning the potential for drift of VOCs under conditions associated with dominant westerly flow of air masses over the Park.

Samples were acquired in the early morning (AM) and again in the early afternoon (PM) at each sample site on February 13 and 16 (Wednesday and Saturday, respectively), 2002, to assess the relative impact of oversnow travel on VOC distributions within the Park. These dates were selected for sampling activity in order to develop a comparison of the spatial variability of VOCs associated with low-to-moderate and high visitation levels. Historically, the month of February is known for high wintertime visitation levels. In February, 1996, average daily visitation was in the range of 1,500 – 1,800 persons [National Park Service, 1999], and NPS documents consistently indicate that the vast majority of wintertime daily visitation is represented by snowmobile trips [National Park Service, 1999; 2000a; 2000b]. Furthermore, personal communication with YNP Planning Staff indicated that the President's Day weekend has historically constituted a high visitation period [J. Sacklin, Personal Communication, 2001].

Although NPS visitation data for the sample dates were not available to the investigators at the time of this report, unconfirmed data that were probably derived from official YNP data indicate that some 1,200 snowmobiles entered the West Entrance on Saturday, February 16, 2002 [*Greater Yellowstone Coalition*, 2002].

Within each daily sample period, samples were acquired within a three-hour period of time. Additionally, a complete set of diurnal samples was acquired every second hour for each day beginning at 12:00 a.m. and ending at 11:59 p.m. at the Lake Ranger Station. This site was selected over the Old Faithful Lodge site in order to better assess VOC dynamics in well mixed air at a more remote location in the Park. Diurnal data corresponding to the AM and PM sample periods on each day were added to their respective data pools.

Ninety-six whole air samples were collected in 1-liter silica lined canisters (Entech Instruments, Simi Valley, CA) and 2-liter electropolished stainless steel canisters (University of California, Irvine, CA). The morning sample collection periods began on at 5 a.m. prior to the initiation of significant oversnow travel and solar loading which can influence the photochemical processing of atmospheric trace gases. Afternoon sampling began approximately at solar noon and extended over a 2-3 hour period of time after which significant oversnow travel had occurred. Due to the apportionment of 2-4 sample sites per field sampler, each sample route or course required a maximum period of 3 hours to complete. The protocol for the collection of well mixed whole air sample for trace gas analysis was strictly followed by each field sampler. All samples were to be collected following a period of several minutes after the shutdown of any research vehicle and at a distance of 50+ m from upwind of all local vehicles and transportation routes. In conjunction with the acquisition of the air samples, data concerning site and canister coding, date and time, topography, wind speed, and ground surface cover were recorded in the Trimble GPS units for each site. In addition, the use of Lowrance® GlobalMap100 GPS units permitted the acquisition of supplementary location data which were manually recorded on data forms together with the basic site data for backup purposes.

In order to compare the relative emissions from two-stroke and four-stroke snowmobiles representative of the rental fleet utilized within the Park, tailpipe exhaust samples were collected from two of the five snowmobiles employed in the field by the research team. Both machines were rented from a commercial snowmobile outfitter located in West Yellowstone, Montana, for the duration of the study period. The sampling methods and analyses for exhaust samples are fully described in Section 3.1 of this report.

The week bracketing the field sampling was dominated by high pressure in YNP. Weak cold fronts passed through the region prior to each sample day bringing clean air from the northwest and scattered dustings of snow. During each day on which samples were collected air was vertically stable with inversions developing during the nighttime hours and lasting well into the short daylight period. Through the period 12:00 a.m. on Wednesday, February 13, to 11:59 p.m. on Saturday, February 16, surface temperatures

ranged from -33 °C (-28 °F) to approximately 0 °C (32 °F) (Table 2). Meteorological observations recorded on Saturday, February 16, at Ranger Stations located within the Park and at the NWS weather station located near the Lake Ranger Station indicated that a slight warming of surface temperatures associated with clear skies produced an increase in elevation of the boundary layer height. However, on neither day was the inversion suspected to have broken. During each day, strong temperature increases of 5-8 °C were noted from hillslope transects. Surface winds were calm or light with mainly a southerly component through the study period, but assumed more of a westerly component as the high-pressure system moved to the southwest. Most collection sites recorded calm conditions or winds of less than 2 miles per hour (1m/sec). Maximum velocities were recorded in gusts at less than 17 miles per hour (8 m/sec) from February 13-16.

Ground surface conditions were characterized by snow cover at all but one site. Snow depths ranged from 48 inches (125 cm) at Grant Village to patchy cover at Mammoth. On Saturday, February 16, the West Entrance recorded a snow depth of 30 inches (76 cm) and 24 inches (51 cm) were recorded at Old Faithful. Due to the low temperatures and limited air exchange, minimal loss of snow cover occurred during the week through either sublimation or melt.

2.2 Trace Gas Analysis

Nonmethane hydrocarbons (NMHCs) and selected halocarbons were measured from the collected whole air samples. The samples were analyzed by trapping 650.0 cm³ (STP) of air on a sample concentration loop, a 1/4-inch O.D. stainless steel loop filled with 1 mm diameter glass beads, immersed in liquid nitrogen. The total volume sampled was measured by pressure difference using a capacitance manometer. After the sample was trapped, the concentration loop was isolated and warmed to 80 °C. When the two gas chromatographs (GCs) reached their appropriate initial temperatures, the sample was injected into the helium carrier flow stream. The carrier stream was then split into two, with each sub-stream feeding a separate GC separation column. One 60 m x 0.25 mm I.D., 1.0 µm film thickness OV-1 column and one 30 m x 0.53 mm I.D., 10 µm film thickness A1₂O₃/Na₂SO₄ PLOT column were used for the trace gas separations. The effluent from the OV-1 column was split, with ~70% of the flow directed to an flame ionization detector (FID) for C₃-C₁₀ NMHC measurements and ~30% to an electron capture detector (ECD) for C₁-C₂ halocarbon measurements. The PLOT column, which was housed in a separate GC, was connected to an FID for C₂-C₆ NMHC measurements. Further information regarding sample analysis and standard calibrations are described in Sive, [1998].

2.3 Spatial Analyses

The geographic locations of sample sites were logged with GeoExplorer 3 GPS devices. Positions constituting individual locations were downloaded into Trimble's[®] GPS Pathfinder Office software (Ver. 2.80) upon the completion of sample collection and were subjected to differential correction via post-processing utilizing base station data for the CORS site at Mammoth, WY (44 58 24.31849 N Lat.; 110 41 21.43409 W Long.)

that were downloaded through the internet. Horizontal accuracy levels for all sample points generally fell under 2 m, and did not exceed 2.3 m. To permit the mapping and spatial analysis of air samples, VOC data for each day's AM and PM sample period were merged with the post-processed and spatially merged GPS data in the GIS environment (i.e., ESRI's ArcView 3.2a). All data were projected in Universal Transverse Mercator units for integration with existing YNP spatial data. The resultant maps (Figures 3-18) portray the mixing ratios in parts per trillion by volume (pptv) of the selected VOCs. Owing to the coarse spatial resolution of the data, VOC concentrations are portrayed cartographically with scaled or graduated point symbols rather than a continuous interpolated surface.

3. Results and Discussion

Approximately 80 NMHCs and 15 halocarbons have been quantified from the 96 whole air samples collected in Yellowstone National Park. In this report, we present some preliminary results using a subset of trace gases measured from the whole air samples. The gases reported here include 14 C₂-C₈ NMHCs (including air toxics such as benzene, toluene and the xylenes) and tetrachloroethene (C₂Cl₄), a good marker for long range transport of urban air. C₂Cl₄ is used to illustrate that urban emissions did not affect the sampling region during the course of our sampling experiment.

3.1 Exhaust Samples

Exhaust samples were collected from a two-stroke and a four-stroke snowmobile in order to compare the relative emission ratios of the two different engine types. The two-stroke exhaust sample was collected from a Polaris Trail Touring snowmobile equipped with a 550 cc fan-cooled engine while the four-stroke exhaust sample was collected from a *Polaris Frontier 4 Stroke* snowmobile equipped with a 780 cc liquidcooled engine. The exhaust samples were collected in 1-liter silica lined canisters (Entech Instruments, Simi Valley, CA) immediately after completing a 75 minute transit from Old Faithful to West Yellowstone. For both snowmobiles, the samples were collected at 5000 RPM, which corresponded to the average revolutions per minute for each engine during the transit. For sample collection, the brake was applied and the engine was held at 5000 RPM while the canister was placed directly into the exhaust stream exiting the tailpipe of each engine and filled to ambient pressure. A 0.5 cm³ (STP) aliquot of each exhaust sample was analyzed by direct injection using the analytical system described previously. From the chromatographic data obtained for these samples, relative emission ratios for each engine type were determined. Results from the exhaust sample analyses indicate that the two snowmobiles sampled had very similar emission ratios for both ethene and ethane. For this comparison, we have normalized the emission ratios to ethene; however, the results do not differ if they are normalized to ethane. The emission ratios relative to ethene for the two-stroke and fourstroke snowmobile engines are illustrated in Figure 2.

Overall, the relative emission ratios for the two-stroke engine are significantly larger for all of the reported compounds (Figure 2). Toluene dominated the two-stroke

engine emissions (approximately five times larger than the four-stroke engine), but relatively large amounts of n-butane, i-pentane and n-pentane were also present in the exhaust sample. For both engine types, only a small fraction of the exhaust consisted of ethane, propane, propene, and i-butane. With regard to air toxic emissions (i.e., benzene, toluene, ethylbenzene and xylenes), the two-stroke engine emitted significantly larger quantities of these gases.

3.2 Overview of Spatial Distributions

The spatial distributions of the 16 reported gases are shown in Figures 3 through 18. Each figure contains four maps corresponding to the morning and afternoon sampling periods during the low and high traffic days (Wednesday and Saturday, February 13 and 16,2002). Mixing ratios are in pptv and are designated by color-coding and symbol size. One feature worth noting before discussing the trace gas spatial distributions is that the road between Silver Gate and Mammoth Hot Springs is used primarily for automobile traffic, as opposed to the remainder of the park roads which are dominated by snowmobile traffic. Therefore, the samples collected in the northern region of the park were generally much cleaner, and the NMHC mixing ratios were only slightly enhanced above background northern hemispheric air.

In order to assist in ruling out the influence of urban emissions on the samples collected in the park, the spatial distribution of C_2Cl_4 was evaluated (Figure 3). For all AM, PM and diurnal samples, the mean C_2Cl_4 mixing ratio and 1σ standard deviation were 7.6 ± 1.1 pptv (the standard deviation at this mixing ratio level is dominated by the instrument's precision). This indicates that there was little or no influence on the air masses sampled in the park from urban areas directly upwind and that the NMHC enhancements observed were representative of local emissions.

The ethane and propane spatial distributions are shown in Figures 4 and 5. For both of these gases, high concentrations were observed at Silver Gate during the morning sampling periods. It is likely that these enhancements were a result of wood burning (used for home heating) and LPG leakage in this area. With the exception of the high values observed in the morning at Silver Gate, the ethane mixing ratios were essentially uniform indicating that the air masses sampled were well mixed throughout the park on both days. Similarly, little variability was observed in the propane mixing ratios during both sampling periods.

Ethene and propene are useful indicators of fresh emissions from combustion sources because of their short atmospheric lifetimes, which are on the order of ~1.5 days and ~0.5 days, respectively. Ethyne, also an indicator of combustion, has an atmospheric lifetime on the order of 2 weeks, resulting in its higher background concentrations. The spatial distributions of these three gases are shown in Figures 6 through 8. As with ethane and propane, the mixing ratios of these gases were also relatively large in the morning samples collected at Silver Gate during both sampling days. However, noticeable enhancements are observed throughout the southern two-thirds for ethene and ethyne during the PM sampling period on both days. Also, enhancements for all three

gases are observed during the PM sampling period at the West Yellowstone entrance. A key feature to note is that the mixing ratios for ethane and ethyne increased between the AM and PM samples. With regard to propene, there is essentially no enhancement throughout the park, especially on the high traffic day, which is consistent with the relatively small fraction of propene emitted from both two-stroke and 4 stroke snowmobiles.

The butanes (i-butane and n-butane) and pentanes (i-pentane and n-pentane) are indicators of fuel evaporation and are also emitted from combustion sources. The spatial distributions of these gases are shown in Figures 9 through 12. For i-butane, the overall difference between the morning and afternoon mixing ratios is small on both days. In contrast to i-butane, the n-butane, i-pentane and n-pentane show large enhancements between the AM and PM sampling periods on each day. The observed enhancements are likely a result of the increased snowmobile usage between the AM and PM sampling periods. However, because the road from Mammoth Hot Springs Silver Gate to is limited to automobiles, the mixing ratios of these gases remain essentially unchanged in this region for all sampling periods. Again, the large enhancements observed for n-butane, i-pentane and n-pentane are consistent with the two-stroke snowmobile exhaust sample.

Similarly, benzene, toluene, ethylbenzene and the xylenes (m-, p- and o-) exhibit spatial distributions comparable to n-butane and the pentanes, with toluene emissions showing the greatest increases between the AM and PM sampling periods (Figures 13 through 18). The potential health hazards associated with exposure to these compounds are the primary reasons for controlling their emissions, thus their classification as federal hazardous air pollutants. The largest mixing ratios (reported here in *parts per billion* by volume, ppbv) observed for each of these compounds were comparable to those found in a polluted urban environment [*Monod et al.*, 2001] illustrating the probable impact of the snowmobile emissions on the airshed. The ratios were as follows: benzene – 4.82 ppbv; toluene – 9.89 ppbv; ethylbenzene – 0.99 ppbv; m-xylene – 3.01 ppbv; p-xylene – 1.37 ppbv; o-xylene – 1.54 ppbv. To put these values into perspective, background mixing ratios for these compounds are expected to be on the order of the following: benzene ~ 100 pptv; toluene ~ 40 pptv; ethylbenzene and the xylenes ~ 5 pptv.

3.3 Comparison of Low and High Traffic Days

Table 3 lists the median and mean mixing ratios in pptv, and percent difference in median mixing ratios between each sampling period to assess the impact of increased snowmobile traffic in the Park.

The decrease in concentration of ethane and propane between the AM and PM sample collections occurs regularly and is associated with the daytime heating of the earth's surface resulting in an increase in the planetary boundary layer height. This indicates that dilution is taking place with clean free tropospheric air mixing into the boundary layer. Even though air mass dilution is occurring, large enhancements in other trace gas mixing ratios associated with local snowmobile emissions were observed. Evaluating the percent difference of the median values for the samples collected on each

day, the impact of the increased number of snowmobiles on the Yellowstone airshed can be assessed (median values are used for comparison rather than mean values so that the results are not skewed by samples with very high concentrations of NMHCs). The compounds listed in Table 3 all show enhancements in the percent difference of the median values between the low-traffic day and high-traffic day except for ethane, propane and C_2Cl_4 . From these results, trace gas emissions from the snowmobile activity can be estimated. Overall, increased snowmobile usage resulted in an increase in median values for the reported trace gases.

4. Conclusions

The findings suggest that, holding overall levels of snowmobile usage steady, a reduction in the amount of two-stroke snowmobile traffic will likely reduce NMHC emissions including the air toxics benzene and toluene. This scenario essentially represents the *Winter Use Plans Draft Supplemental Environmental Impact Statement*'s Alternative 2. Alternatives 1a, 1b, and 3 will lead to significant decreases NMHC and air toxic levels in the Park.

5. Appendices

5.1 Tables

Table 1. Sample Sites and Codes

Table 1. Sample Sites and Codes				
Sample Site	Site Code			
Mammoth Hot Springs	A1			
5 km West of Tower Junction	A2			
Mammoth-Cooke City Rd 1 km West of Soda Butte	A3			
Cr./Lamar R. Confluence				
Silver Gate	A4			
Mud Volcano	B1			
Canyon	B2			
Norris Geyser Basin	В3			
Yellowstone Lake Overlook	C1			
East Entrance	C2			
Old Faithful Lodge Area	D1			
Fountain Paint Pots	D2			
Madison River Bridges	D3			
1 km South of West Yellowstone in Gallatin National	D4			
Forest				
Old Faithful-Grant Village Rd Continental Divide	E1			
(Eastern-most)				
Grant Village	E2			
Grant Village-South Entrance Rd. – Approx. 8 km South	E3			
of Lewis Lake				
Lake Ranger Station	DIURNAL			

Table 2. Yellowstone Lake, WY Weather Conditions

Date	Min. Temp. F (C)	Max. Temp. F (C)	Min. Pressure. In (mbs)	Max. Pressure In (mbs)	Predominant Winds 7 am 1pm	
Wednesday February 13 th	-15 (-26)	24 (-4.4)	29.9(1012)	30.35(1027)	Calm	Calm
Saturday February 16 th	-18 (-28)	26 (-3.3)	30.08(1018)	30.35(1027)	Calm	Calm

Table 3. Median and mean mixing ratios along with the percent difference in median values between morning and afternoon sampling times are reported for all samples collected throughout the park on the low traffic day (2/13/02) and high traffic day (2/16/02). All values were calculated using 14, 17, 16 and 17 samples for the 2/13/02 am, pm and 2/16/02 am, pm periods, respectively. On both days, morning samples were collected between 5 am and 7 am while afternoon samples were collected between 12 pm and 2 pm. All mixing ratios are reported in pptv.

		Sample [*]			G
Compound	Date	Time	Median	Mean	% Difference
ethane	2/13/2002	am	1964.4		
		pm		1974.5	-7%
	2/16/2002	am		1967.1	
		pm	1627.3	1732.2	-10%
athana	2/42/2002		407.0	400.4	
ethene	2/13/2002	am	197.3 159.6	420.1 825.6	-24%
	2/16/2002	pm am	104.1	835.6	-2470
	2/10/2002	pm	224.5	508.6	54%
		Pili	224.0	000.0	0470
ethyne	2/13/2002	am	432.0	553.7	
		pm	450.8	761.8	4%
	2/16/2002	am	358.2	669.3	
		pm	447.0	869.4	20%
propane	2/13/2002	am	672.5	1888.7	
	0/40/0000	pm	662.5	894.8	-2%
	2/16/2002	am		2708.1	050/
		pm	470.0	585.3	-25%
propene	2/13/2002	am	49.5	164.6	
properie	2/10/2002	pm	74.1	396.4	33%
	2/16/2002	am	38.5	336.9	0070
	_, . 0, _ 0 0 _	pm	103.8	209.9	63%
		•			
i-butane	2/13/2002	am	128.6	179.0	
		pm	139.7	1206.8	8%
	2/16/2002	am	91.9	146.3	
		pm	145.6	260.7	37%
n_butone	2/13/2002	am	281.7	431.2	
n-butane	2/13/2002	am pm		431.2 2967.5	20%
	2/16/2002	am	213.8	365.3	20 /0
	2/10/2002	pm	345.3	918.0	38%
		F ***			· -
i-pentane	2/13/2002	am	60.3	166.6	
		pm	121.9	1775.3	51%
	2/16/2002	am	46.6	181.1	
		pm	158.9	453.0	71%
n nontono	2/42/2022	0.00	E0.0	07.0	
n-pentane	2/13/2002	am	50.2 68.5	97.3	270/
	2/16/2002	pm am	35.2	1033.1 114.5	27%
	2/10/2002	pm	100.9	241.0	65%
	1	Pill	100.9	Z-71.U	00 /0

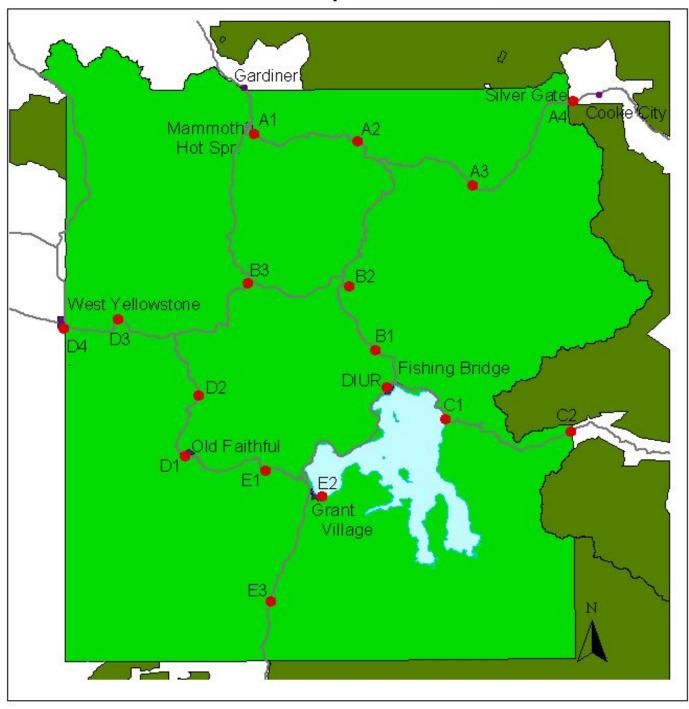
 $Table\ 3\ (continued).\ Median\ and\ mean\ mixing\ ratios\ for\ selected\ compounds\ along\ with\ the\ percent\ difference\ in\ median\ values\ between\ morning\ and\ afternoon$

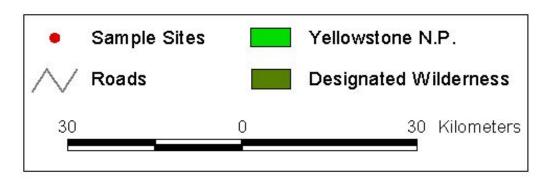
sampling times.

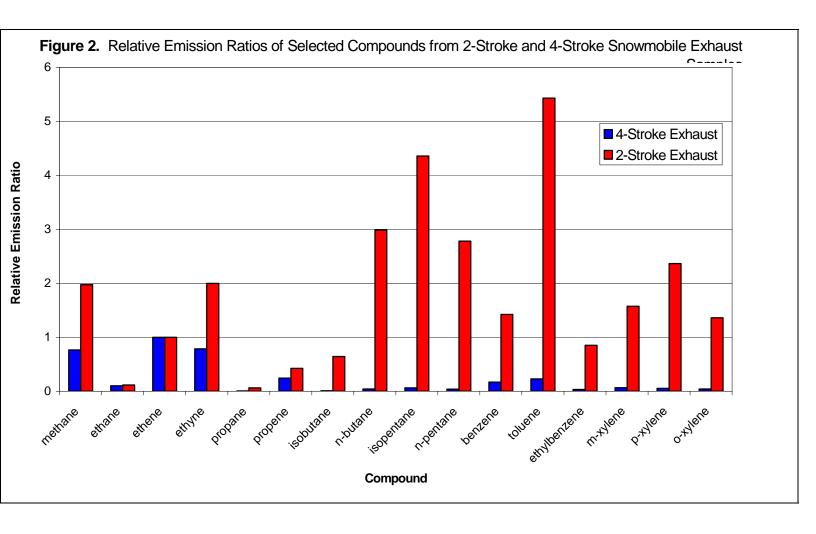
Compound	Date	Sample Time	Median	Mean	% diff Med Values
benzene	2/13/2002	am	181.3	507.8	
		pm	156.1	420.4	-16%
	2/16/2002	am	147.6	241.0	
		pm	200.5	396.4	26%
toluene	2/13/2002	am	124	220	
		pm	149	1090	17%
	2/16/2002	am	98	277	
		pm	259	1205	62%
ethylbenzene	2/13/2002	am	10.5	25.7	
		pm	16.3	114.4	36%
	2/16/2002	am	9.7	28.7	
		pm	27.6	117.3	65%
m-xylene	2/13/2002	am	25.5	53.6	
		pm	21.3	302.3	-20%
	2/16/2002	am	28.5	65.9	
		pm	60.8	324.3	53%
p-xylene	2/13/2002	am	15.0	30.9	
		pm	30.9	171.4	51%
	2/16/2002	am	15.5	48.8	
		pm	44.2	107.9	65%
o-xylene	2/13/2002	am	18.4	34.5	
		pm	41.4	199.6	56%
	2/16/2002	am	18.4	40.5	
		pm	42.6	185.1	57%
C ₂ CI ₄	2/13/2002	am	8.1	8.4	
		pm	8.5	8.5	4%
	2/16/2002	am	7.4	7.2	
		pm	6.6	6.7	-12%

5.1 Figures

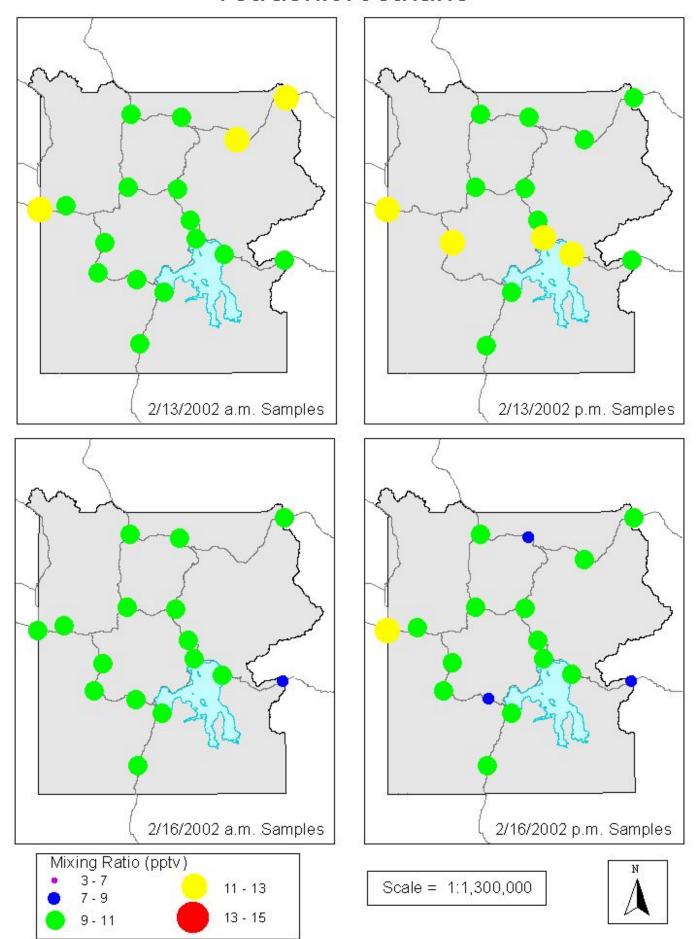
Sample Sites



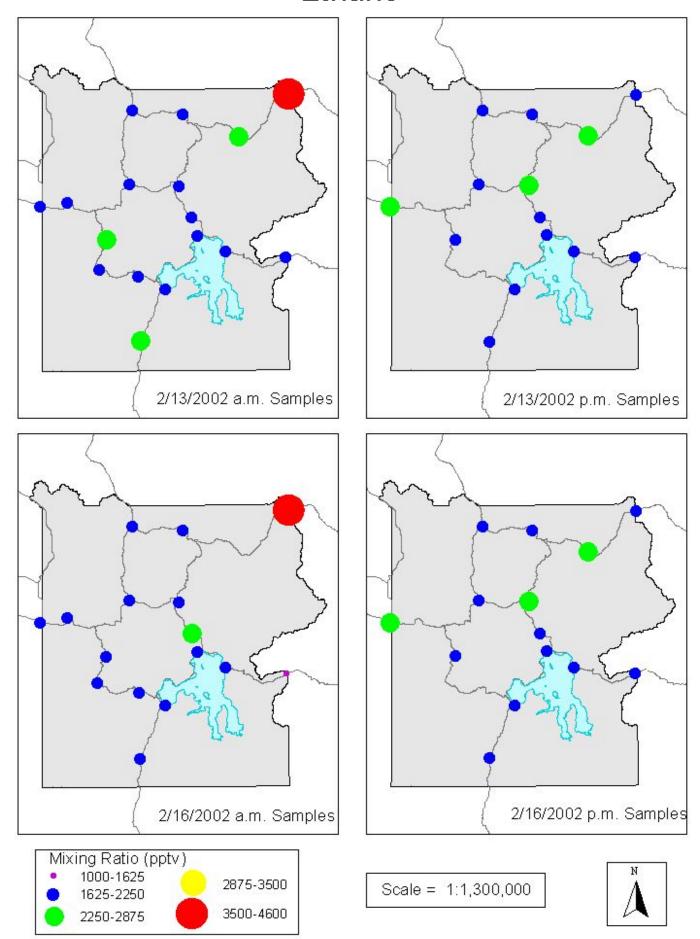




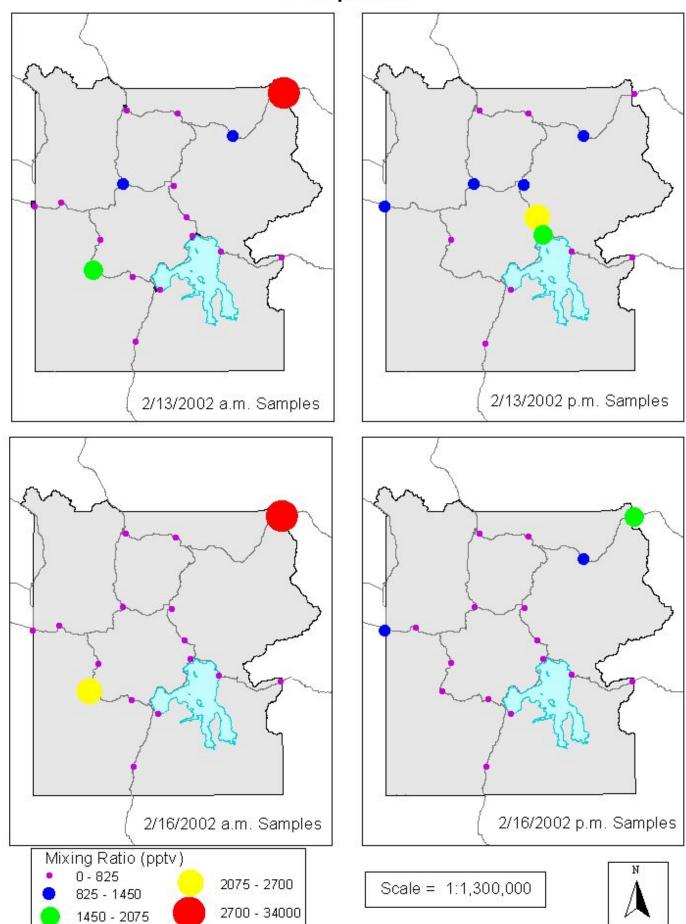
Tetrachloroethane



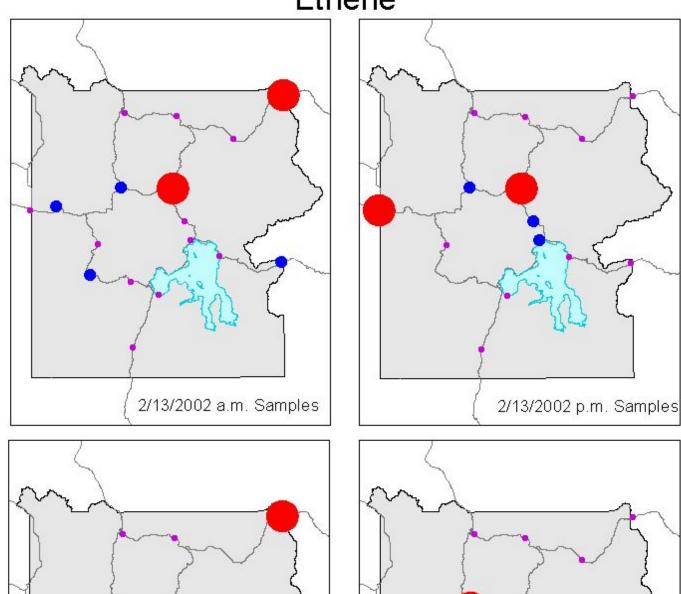
Ethane

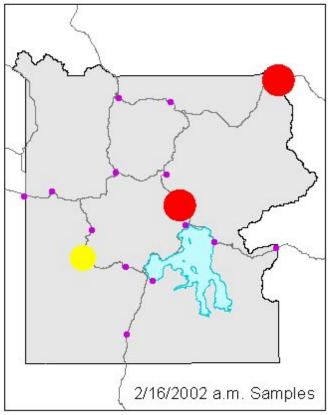


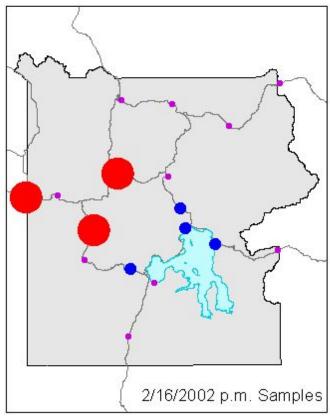
Propane

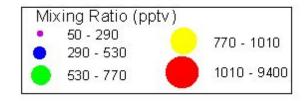


Ethene





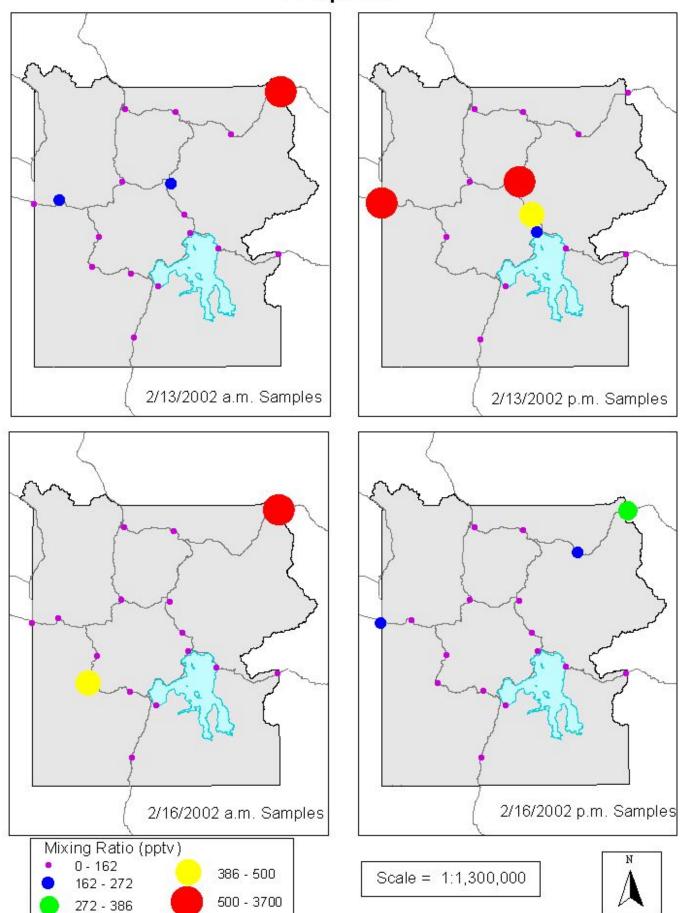




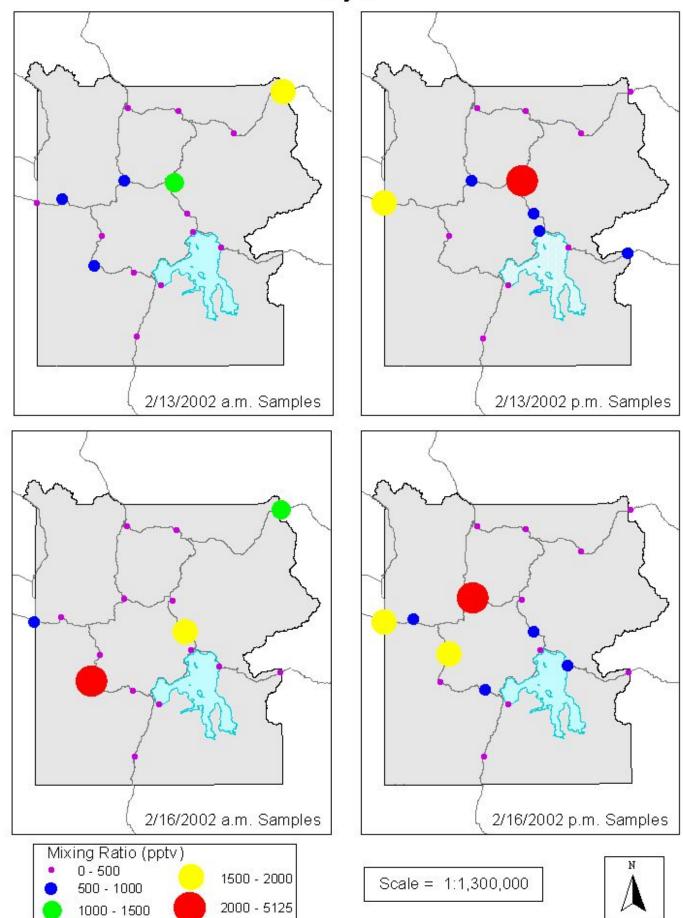
Scale = 1:1,300,000



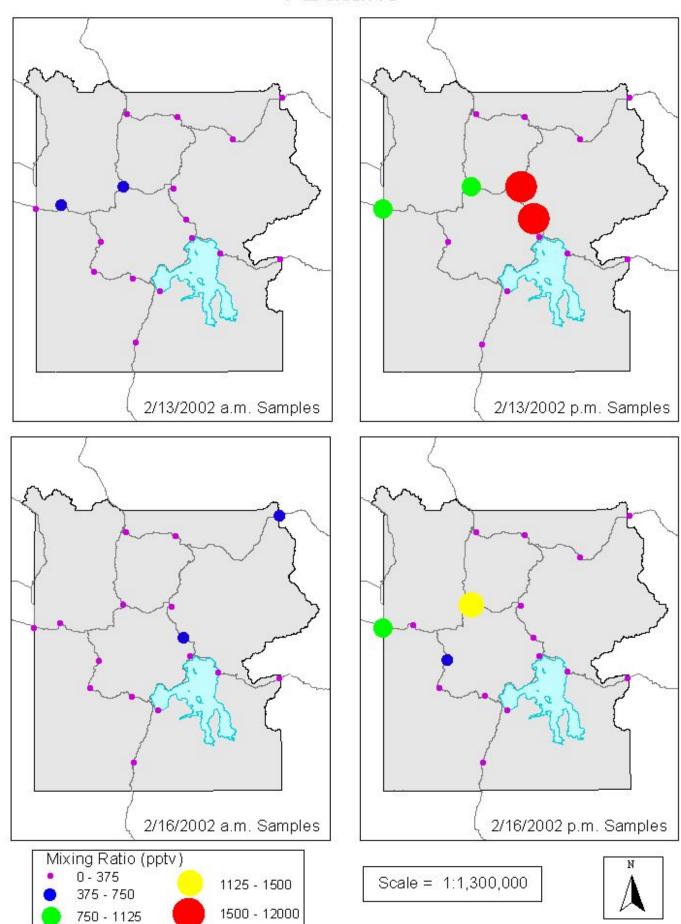
Propene



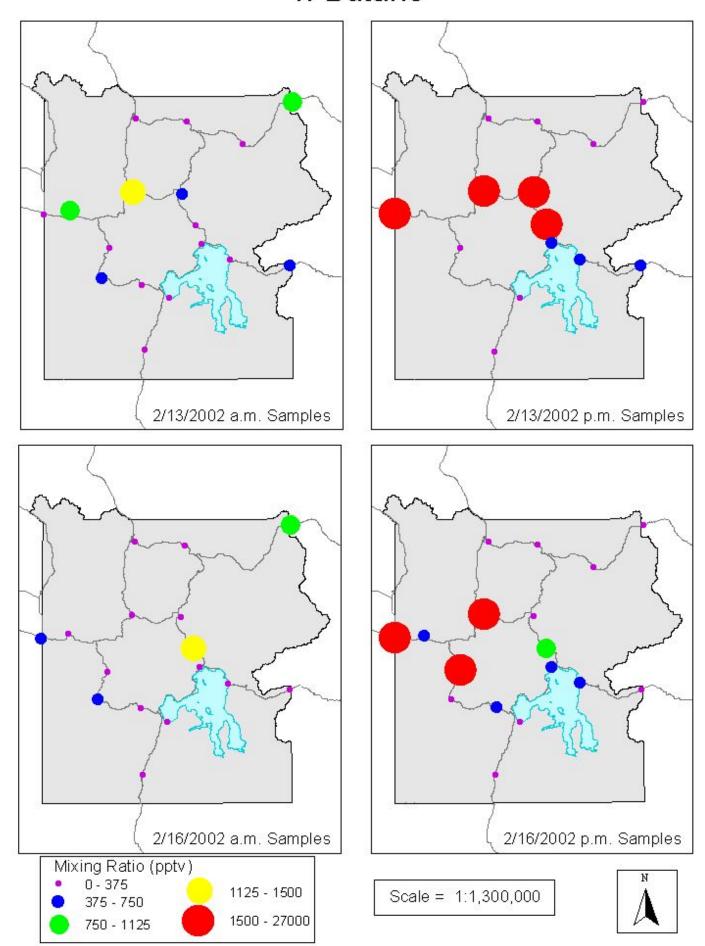
Ethyne



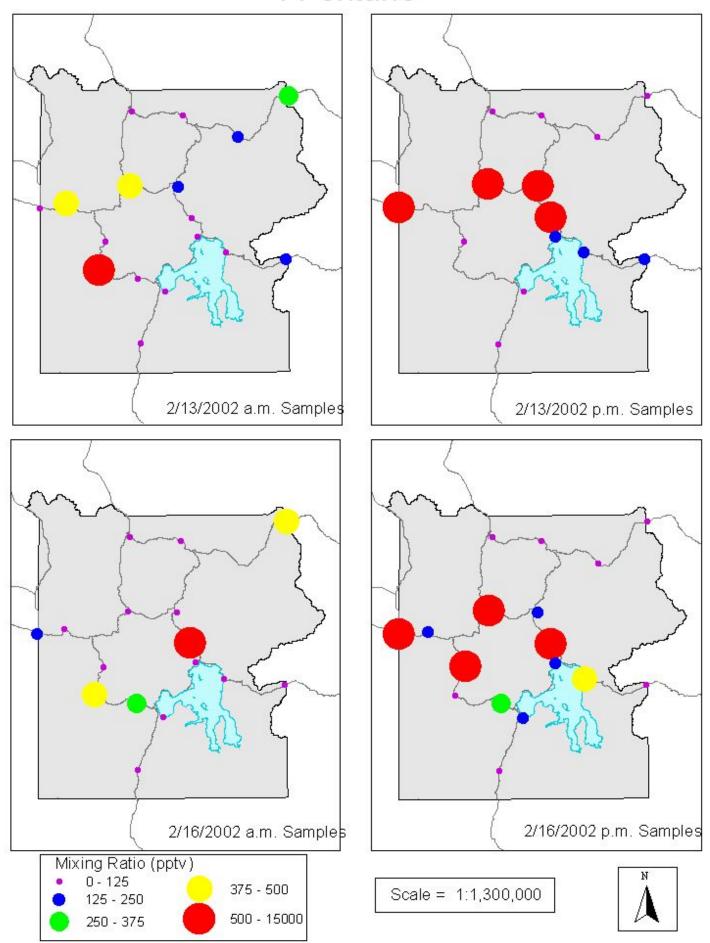
i-Butane



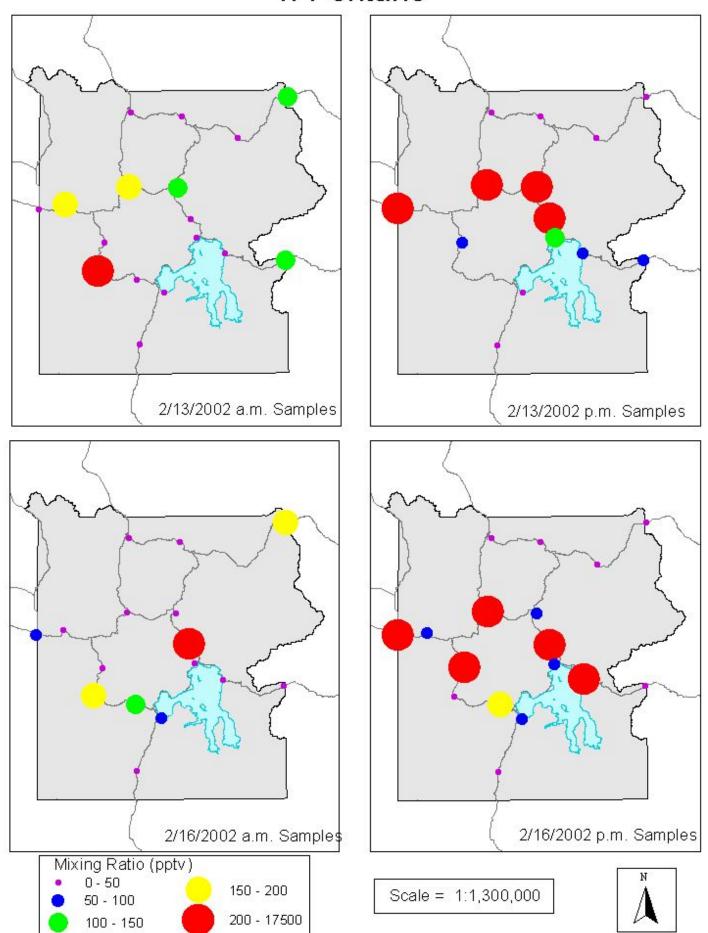
n-Butane



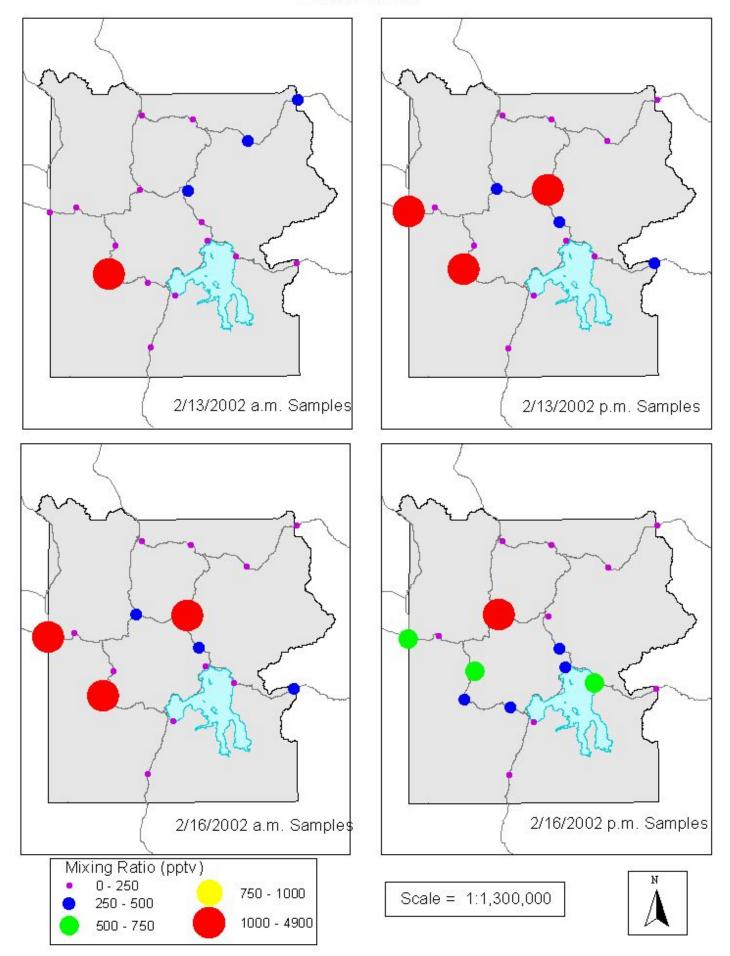
i-Pentane



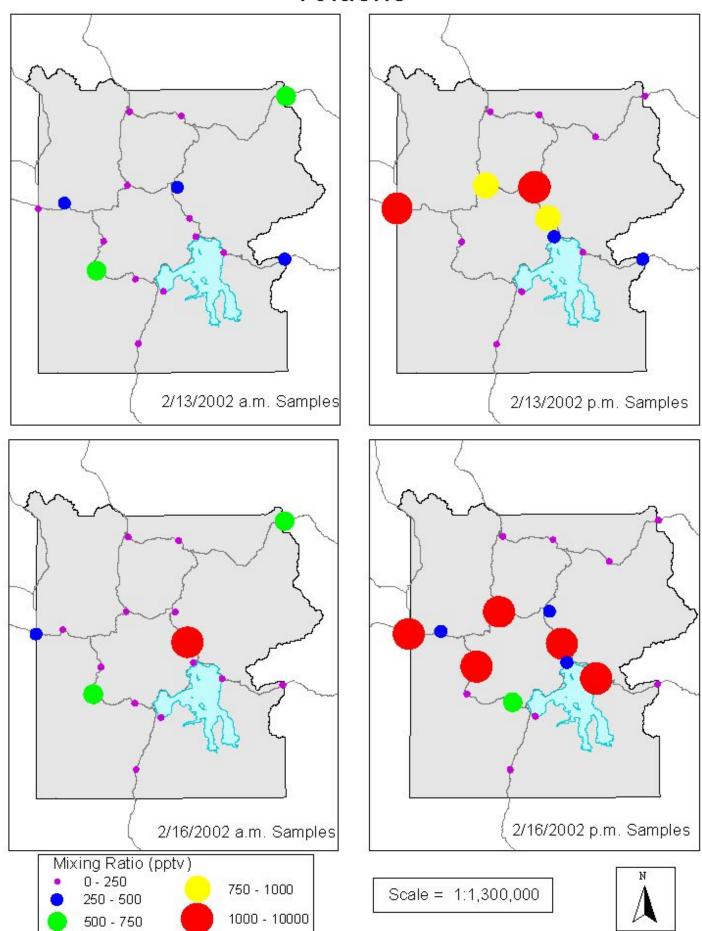
n-Pentane



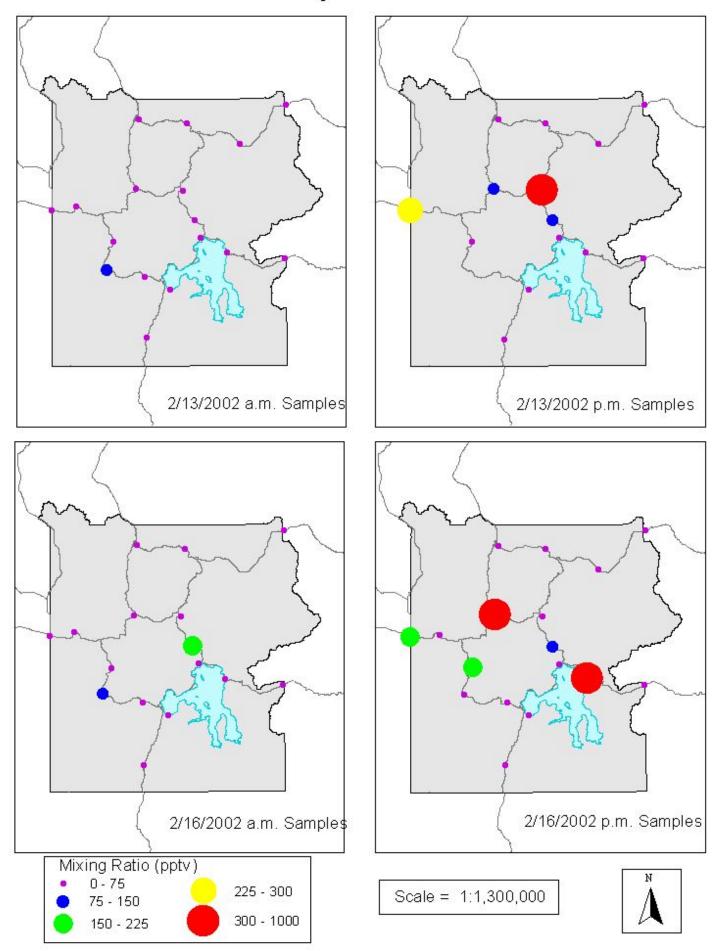
Benzene



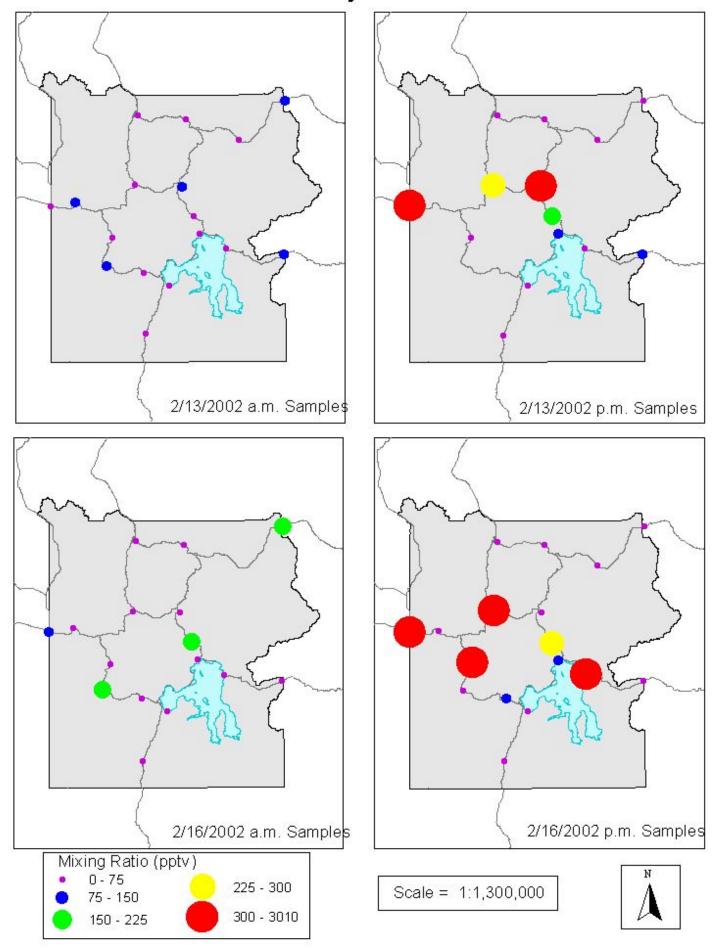
Toluene



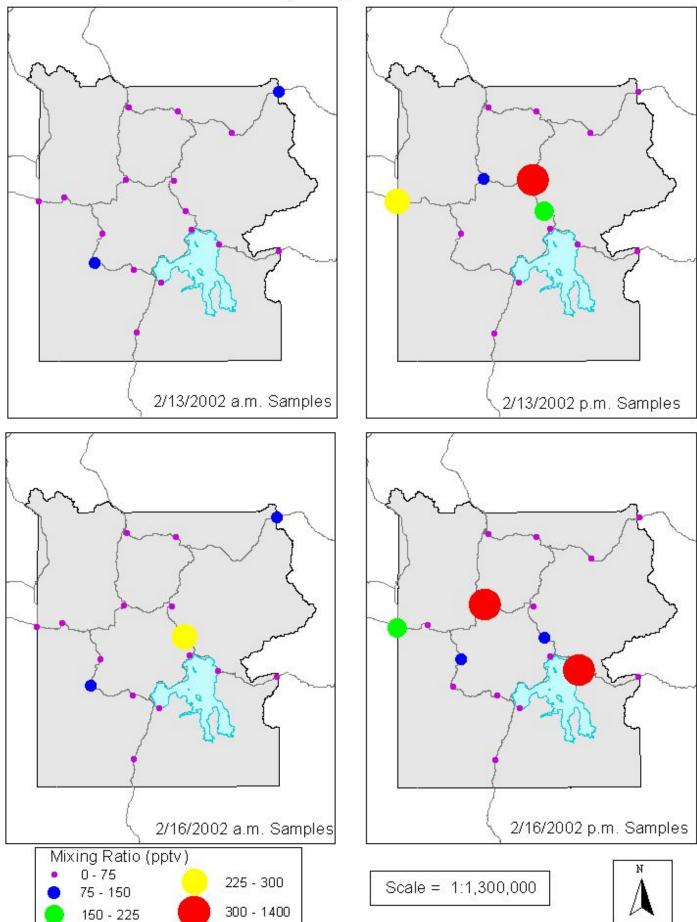
Ethylbenzene



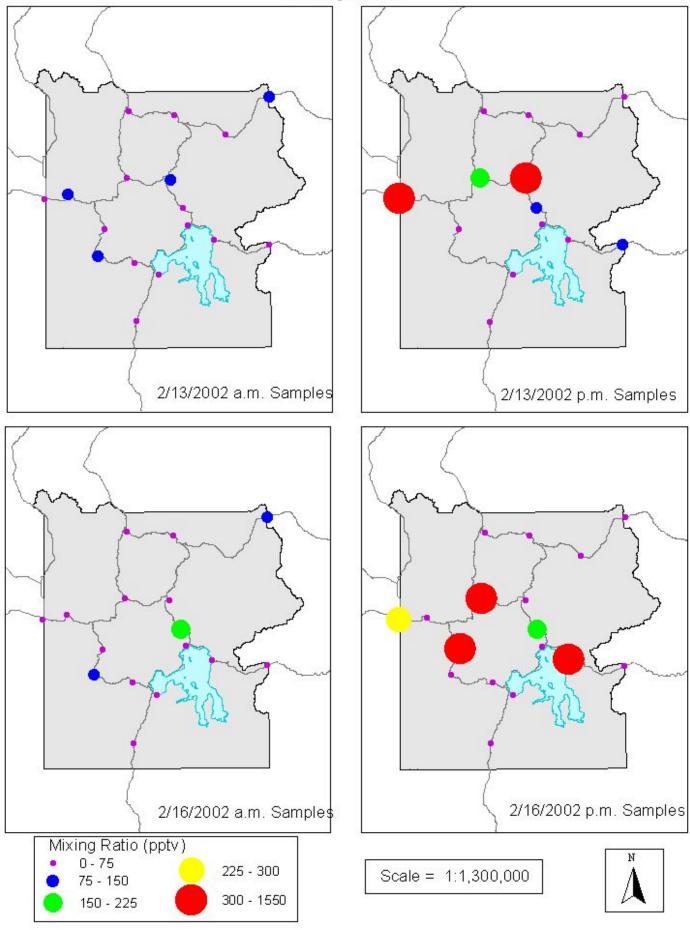
m-Xylene



p-Xylene



o-Xylene



5.3 Literature Cited

- Air Resource Specialists, Inc. 1996. Carbon Monoxide and Particulate Matter Levels at Yellowstone National Park, West Entrance Station: Results of an Ambient Air Quality Study, Winter 1995, Draft Report prepared for the National Park Service, 1995.
- Ariya, P. A., R. Sander, and P. J. Crutzen, Significance of HOx and peroxides production due to alkene ozonolysis during fall and winter: A modeling study, *J. Geophys. Res.*, 105, 17721-17738, 2000.
- Bishop, G. A., J. A. Morris, and D. H. Stedman, Snowmobile contributions to mobile source emissions in Yellowstone National Park, *Environ. Sci. Techol.*, *35*, 2874-2881, 2001.
- Blake, D. R., T. Y. Chen, T. W. Smith, Jr., C. J.-L. Wang, O. W. Wingenter, N. J. Blake, F. S. Rowland, and E. W. Mayer, Three-dimensional distribution of NMHCs and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A), *J. Geophys. Res.*, 101, 1763-1778, 1996.
- Carroll, J. N., and J. J. White, *Characterization of Snowmobile Particulate Emissions*, Final Letter Report prepared for Yellowstone Park Foundation, Inc., Southwest Research Institute, San Antonio, TX, 1999.
- Goldan, P. D., W. C. Kuster, and F. C. Fehsenfeld, Nonmethane hydrocarbon measurements during the Tropospheric OH Photochemistry Experiment, *J. Geophys. Res.*, 102, 6315-6324, 1997.
- Greater Yellowstone Coalition. *Snowmobiles*, available: http://www.greateryellowstone.org/act_snowmobiles.html, May, 26, 2002.
- Hagemann, M., and M. VanMouwerik, Potential water quality concerns related to snowmobile usage, National Park Service, Water Resources Division, 1999.
- Ingersoll, G., Effects of snowmobile use on snowpack chemistry in Yellowstone National Park, 1998, USGS, Department of Interior, *Water-Resources Investigation Report* 99-4148, 1999.
- Ingersoll, G., J. Turk, C. McClure, S. Lawlor, D. Clow, and A. Mast, Snowpack chemistry as an indicator of pollutant emission levels from motorized winter vehicles in Yellowstone National Park, *Proceedings of 65th Annual Meeting of Western Snow Conference*, May 4-8, 1997, Banff, Alberta, 1997.
- Institute for Environment and Natural Resources, Review of Research Related to the Environmental Impact Statement for the Yellowstone and Grand Teton National Parks and the John D. Rockefeller, Jr. Memorial Parkway, Report prepared by the University of Wyoming for the State of Wyoming Department of State Parks and Cultural Resources, 2000.
- International Agency for Research on Cancer (IARC), IARC Monographs on the Evaluation of Carcinogenic Risks to Humans: Overall Evaluation of Carcinogenicity: An Updating of IARC Monographs Vol 1-42, Supplement 7, World Health Organization, Lyon, France, 1987.
- Irwin, R. J., M. VanMouwerik, L. Stevens, M. D. Seese, and W. Basham, Environmental Contaminants Encyclopedia, National Park Service, Water Resources Division, Fort Collins, Colorado, 1998.

- Kado, N. Y., P. A. Kuzmicky, and R. A. Okamoto, Measurement of Toxic Air Pollutants Emitted from Snowmobiles at Yellowstone National Park, Draft Report prepared for the Yellowstone Park Foundation, Pew Charitable Trust, and National Pak Service, Department of Environmental Toxicology, University of California, Davis, 1999.
- Keller, A. et al., Health and Environmental Assessment of MTBE: Report to the Governor and Legislature of the State of California as Sponsored by SB 521, Volume I, Summary and Recommendations, University of California, Davis, 63, 1998.
- Lamanna, M. S., A. H. Goldstein, In situ measurements of C₂-C₁₀ volatile organic compounds above a Sierra Nevada ponderosa pine plantation, *J. Geophys. Res.*, 104, 21,247-21,262, 1999.
- Lippman, M., Health effects of ozone, J. Air Waste Manage. Assoc., 39, 672, 1989.
- Lippman, M., Health effects of tropospheric ozone, Environ. Sci. Techol., 25, 1954, 1991.
- Morris, J. A., G. A. Bishop, and D. H. Stedman, Real-time Remote Sensing of Snowmobile Emissions at Yellowstone National Park: An Oxygenated Fuel Study, 1999, Draft Report, 1999.
- Monod, A., B.C. Sive, P. Avino, T. Chen, D.R. Blake, and F.S. Rowland, Monoaromatic compounds in ambient air of various cities: a focus on correlations between the xylenes and ethylbenzene, *Atmos. Environ.*, *35*, 135-149, 2001.
- National Park Service, Ambient Air Quality Study Results: West Entrance Station, Yellowstone National Park, Winter 1995, Unpublished Report, 1995.
- National Park Service, Winter 1996 Carbon Monoxide Monitoring, West Entrance and West Entrance road, Yellowstone National Park, Unpublished Report, 1996.
- National Park Service, *Yellowstone National Park*, 1999. The State of the Park, Mammoth Hot Springs: Wyoming, 1999.
- National Park Service, Record of Decision: Winter Use Plans for Yellowstone and Grand Teton National Parks and the John D. Rockefeller Jr., Memorial Parkway, U.S. Department of the Interior, National Park Service, Intermountain Region, 2000a.
- National Park Service, Winter Use Plans Final Environmental Impact Statement for the Yellowstone and Grand Teton National Parks and John D. Rockefeller, Jr., Memorial Parkway, Prepared by the U.S. Department of Interior, National Park Service in cooperation with the U.S. Forest Service; the States of Idaho, Montana, and Wyoming; and the Counties of Gallatin and Park, Montana, Park and Teton, Wyoming, and Fremont, Idaho, 2000b.
- National Park Service, Air Quality Concerns Related to Snowmobile Usage in National Parks. Air Resources Division, National Park Service, Denver, 2000c.
- National Park Service, Winter Use Plans –Draft Supplemental Environmental Impact Statement for the Yellowstone and Grand Teton National Parks and John D. Rockefeller, Jr., Memorial Parkway, Prepared by the U.S. Department of Interior, National Park Service in cooperation with the U.S. Forest Service, the States of Montana, Wyoming and Idaho, and the Counties of Gallatin and Park in Montana, Park and Teton in Wyoming, 20002.
- Radke, T., *Industrial Hygiene Consultation Report*, Report 970101 prepared for Yellowstone National Park, Department of Interior, Office of Managing Risk and Public Safety, Lakewood, CO, 1997.

- Riemer, D., W. Pos, P. Miline, C. Farmer, R. Zika, E. Apel, K. Olszyna, T. Kleindienst, W. Lonneman, S. Bertman, P. Shepson, and T. Starn, Observations of nonmethane hydrocarbons and oxygenated volatile organic compounds at a rural site in the southeastern United States, *J. Geophys. Res.*, 103, 28,111-28,128, 1998.
- Rowland, F. S., N. R. P. Harris, and D. R. Blake, *Nature*, 347, 432-433, 1990.
- Seila, R. L., and W. A. Lonneman, paper 88-150.8, 81st Annual Meeting of the Air Pollution Control Association, Dallas, Texas, June 20-24, 1988; quoted in J. H. Seinfeld, Science, 243, 745-753, 1988.
- Seinfeld, J. H., and S. N. Pandis, *Atmospheric Chemistry and Physics, From Air Pollution to Climate Change*, John Wiley, New York, 1998.
- Sive, B. C., Atmospheric NMHCs: Analytical methods and estimated hydroxyl radical concentrations, Ph.D. Thesis, University of California, Irvine, 1998.
- Snook, L. M., and W. T. Davis, *An Investigation of Driver Exposure to Carbon Monoxide While Traveling in the Wake of a Snowmobile*, Report 97-RP143.02, Air & Waste Management Association's 90th Annual Meeting and Exhibition, June 8-13, Toronto, 1997.
- U. S. Department of Interior. Winter Use Plans Supplemental Draft Environmental Impact Statement For the Yellowstone and Grand Tetons National Parks and John D. Rockefeller, Jr., Memorial Parkway. Prepared March 29, 2002.
- U.S. EPA, *Air Toxics from Motor Vehicles*, EPA 400-F-92-004, U.S. EPA, Office of Mobile Sources, Ann Arbor, Michigan, 3, 1994.
- White, J. J., and J. N. Carroll, *Emissions from Snowmobile Engines Using Bio-based Fuels and Lubricants*. Prepared for the Montana Department of Environmental Quality, by Southwest Research Institute, Report number SwRI 7383, 53, 1998.
- Wingenter, O. W., M. K. Kubo, N. J. Blake, T. W. Smith, Jr., D. R. Blake, and F. S. Rowland, Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights, *J. Geophys. Res.*, 101, 4331-4340, 1996.
- Wright, C. W., and J. J. White, Development and Validation of a Snowmobile Engine Emission Test Procedure, SAE Technical Paper 982017, International Off-Highway & Powerplant conference & Exposition, Milwaukee, WI, September 14-16, 1998.